Decontamination of real textile industrial effluent by strong oxidant species electrogenerated on diamond electrode: Viability and disadvantages of this electrochemical technology

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A B S T R A C T

In a previous work [1], the treatment of dye solutions containing Remazol Red BR (RRB) and Novacron Blue C-D (NB) by anodic oxidation using boron doped diamond anode (BDD) demonstrated that the electrochemical treatment is an efficient alternative for removing color and chemical oxygen demand (COD) and this technology can be used for depuration of real effluents. More recently, these assumptions have been confirmed by oxidizing electrochemically a real textile effluent using BDD anode [2]. Then, as a further development of the research carried out in these previous studies [1,2], in the present work, it has been considered appropriate to extend the investigation to the anodic oxidation, using BDD anode, of a specific real effluent discharged by Brazilian textile industry, adding Na_2SO_4 or NaCl salts in order to verify the applicability of this treatment producing in situ strong oxidant species (peroxodisulfates or active chlorine, respectively).

In this study, we also attempt to discuss critical evidence about the viability of peroxodisulfates or active chlorine. Results obtained in this research clearly demonstrated that the effect of the electrogenerated strong oxidant species, peroxodisulfates or active chlorine, depends on electrocatalytic mechanism followed on BDD surface, improving the color and COD removal. However, there is a limit of NaCl for treating real effluents avoiding the formation of organochloride compounds; and it is a subject of critical importance, from the environmental point of view, to apply this alternative treatment.

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1. Introduction

In the last years, many research groups have demonstrated that boron-doped diamond (BDD) anodes allow complete mineralizations up to near 100% of current efficiency (because it has several technologically important characteristics including an inert surface with low adsorption properties, remarkable corrosion stability even in strongly acidic media and extremely high O_2 evolution overvoltage) of a large number of organic pollutants, such as carboxylic acids, benzoic acid, cyanides, cresols, herbicides, drugs, naphthol, phenolic compounds, polyhydroxybenzenes, polyacrylates, surfactants, etc.; as summarized and discussed by authoritative reviews [3–7].

A considerable number of laboratories have also investigated the applicability of BDD anodes for the electrochemical treatment of wastewaters and the number of related publications has increased rapidly [6]. Among them, the electrochemical treatment of aqueous wastes containing dyes (dyes solutions, synthetic and actual wastewaters) have created great interest [8] because BDD anode has been defined as non-active electrode, since it is expected that it do not provide any catalytically active site for the adsorption of reactants and/or products in aqueous media [6]. Hydroxyl radical (BDD(•OH)) formed from water discharge on its surface from reaction: $H_2O \rightarrow {}^{\bullet}OH + e^- + H^+$, is then considered the responsible species for the electrochemical combustion of organic pollutants, although slower reactions with other reactive oxygen species (H_2O_2 and O_3) and electrogenerated oxidants (active chlorine, peroxodisulphate, peroxodicarbonate or peroxodiphosphate) are also feasible [3,5–7].

Taking into consideration the above information, many electrochemical studies for depuration of wastewaters containing dyes (dyes solutions, synthetic and real textile effluents) have been performed for studying the influence of chloride, sulphate and phosphate in the depuration rate process using BDD anodes

[3,8–14]. However, no attempts have been published concerning to the electrochemical treatment of real textile effluent, comparing the efficiency of the strong oxidant species produced in situ and their disadvantages. For these reasons, this research aims to test the performance of electrochemical treatment process using BDD anodes as an alternative to treat a real textile effluent in order to reduce dye-contamination and strong color, comparing the influence of the strong oxidant species electrogenerated on its surface (peroxodisulfates or active chlorine) and getting more attention on the intermediates produced during degradation to determine its environmental viability.

2. Materials and methods

2.1. Real effluent characteristics

The effluent sample was mainly composed of Remazol Red BR (RRB), Novacron Blue C-D (NB), amylum and different additives (specific textile coloration process involving NB and RRB; two dyes widely used in a Northeast Brazilian Textile industry [1]). This effluent contained a high concentration of COD (1018 mg dm^{-3}) and Hazen Units (7504 HU). Its conductivity was 5.90 mS cm^{-1} and pH was around 12.4. It is worth noting that these conditions were determined from the effluent without any physical–chemical treatment (effluent directly obtained after textile coloration process).

2.2. Electro-oxidation experiments

Bulk oxidations were carried out in an undivided electrochemical cell, the reaction compartment having a capacity of 0.5 L. The anodic oxidation experiments of real textile effluent were performed under galvanostatic conditions using a VERSTAT3-galvanostat (Princeton Applied Research). BDD anode (synthesized as described in Ref. [15]) was supplied by Adamant Technologies (Neuchatel, Switzerland). BDD was used as the anode, and titanium as the cathode. Both electrodes were square, each with 10 cm^2 geometrical area. Experiments were performed at 25 °C for studying the role of salts dissolved in the effluent by applying current densities (j) of 20, 40 and 60 mA cm^{-2}, while the temperature effect (25, 40 and 60 °C) was studied under current densities of 40 and 60 mA cm^{-2}. The temperature of the electrolyte was controlled using a water thermostat.

2.3. Analytical methods

Color removal was monitored by measuring absorbance decrease; using a UV 1800 Shimadzu spectrophotometer. Experimentally, decolorization process was determined by the expressions (1) and (2) reported in the first part of this work [1]. Hazen Units (HU) were determined using a spectrophotometer (Hach Model DR/2500) calibrated with a method 8025 (Pt–Co units) [16]. pH variation was measured using a Methrom pH meter. Decontamination of real effluent was monitored from the abatement of their COD. Values were obtained, using a HANNA HI 83099 spectrophotometer after digestion of samples in a HANNA thermo-reactor. The energy consumption was estimated considering the volume of effluent treated (kWh m^{-3}). The average cell voltage during the electrolysis is taken into consideration for calculating the energy consumption by expression reported in previous works [1,2]. The production of strong oxidants peroxodisulfates and active chlorine were confirmed for some experiments using the I$_2$/I$^-$ titration and the N,N–diethyl-p-phenylenediamine (DPD) colorimetric methods, respectively [17,18].
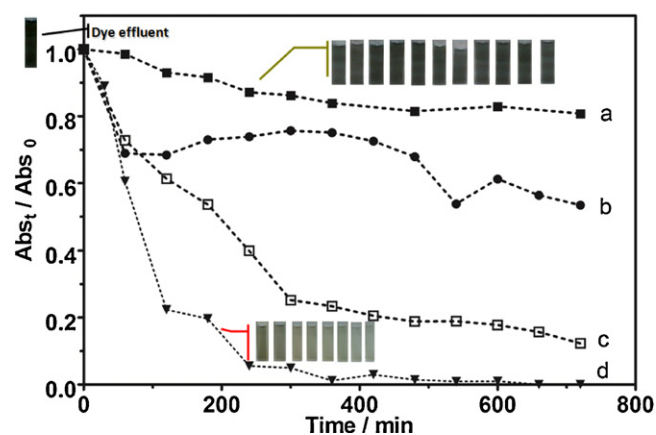

Fig. 1. Electrochemical decolorisation process of a real effluent, as a function of time, applying different current densities values at 25 °C (curve a: 60 mA cm^{-2}, effluent as obtained; curve b: 20 mA cm^{-2}, 5 g of Na$_2$SO$_4$; curve c: 40 mA cm^{-2}, 5 g of Na$_2$SO$_4$ and curve d: 60 mA cm^{-2}, 5 g of Na$_2$SO$_4$). Inset: photographs showing color removal.

3. Results and discussion

3.1. Electrochemical treatment of a real textile effluent un-additional salts (as obtained from industry)

In the first part of this work [1], we have studied the application of the electrochemical oxidation of synthetic dye wastewaters (Remazol Red BR (RRB) and Novacron Blue C-D (NB)) using a BDD anode. This anode evidenced its great oxidation ability to remove the dissolved organic pollutants, requiring shorter electrolysis time to reach overall mineralization, leading higher current efficiencies and lower specific energy consumptions.

The good removal efficiencies suggest the possibility for using electrochemical oxidation as technology for treating real textile effluents. In fact, this anode has been previously used to treat electrochemically textile effluents [2,14,19]. However, each effluent was different, for this reason, it is not easy to compare the results. Then, a specific effluent of an actual Brazilian textile industry was employed to assess the efficiency on electrochemical treatment (using BDD anodes) as an alternative for removing organic matter and color.

As shown in Fig. 1 (curve a), the decrease of the absorbance, as a function of time, during galvanostatic electrolysis of real textile effluent (0.5 L) was monitored for the period of 12 h by applying 60 mA cm^{-2} of current density under original discharged effluent conditions ($T = 25°$). However, the Brazilian regulations [20] for color removal were not attained under these circumstances. No more than partial color removal was achieved ($\approx$21% (5940 HU, see photos)), due to the low conductivity of the effluent and higher organic pollutant concentrations dissolved in the effluent (NB, RRB amylum and different additives), which increases the decolorisation time required for complete elimination. On the other hand, COD was partially removed, decaying from 1018 mg dm^{-3} to 890 mg dm^{-3}, approximately 12.6%.

The effect of temperature was also studied, at 60 °C by applying 60 mA cm^{-2}, mimicking the real temperature utilized to discharge effluents by the textile industry. It was observed that increasing the effluent temperature from 25 °C to 60 °C, the COD abatement remains very similar. This can be justified because the effects are expected to be merely due to hydroxyl radicals generated at the electrode surface, and changes of temperature affect incineration rate through the electrochemical water oxidation together with the parasite reactions consuming OH radicals.

Although the applicability of this treatment seems feasible, long time would be required to complete decolorisation and organic

matter removal (more than 48 h). However, as proved by results presented in previous papers [1,2], the color and COD can be completely removed by anodic oxidation using BDD anode thanks to the effective generation of oxidant species (hydroxyl radicals, active chlorine and peroxodisulphates [2,14,15,17]) on its surface.

For this reason, a new set of experiments was performed to increase the understanding of real effluent treatment by involving the electrochemical production of reactive oxidant species (peroxodisulphates or active chlorine). Taking into account the above information, two questions are also addressed in this work:

(1) What is the most efficient mediated electrochemical oxidation, peroxodisulfates or active chlorine?
(2) Is it possible that the use of peroxodisulfates or active chlorine may result in generation of undesired by-products?

To address these questions, we compare the results obtained using both reactive oxidant species, under different temperatures and concentrations and by analysing the generation of by-products at the end of electrochemical treatment.

3.2. Electrochemical treatment of a real textile effluent adding Na_2SO_4

Electrooxidation experiments were performed in order to understand the role of sulphate addition for complete color and COD elimination. Firstly, an amount of Na_2SO_4 (5 g) was dissolved in the real effluent (0.5 L), in other words, the concentration of Na_2SO_4 in the effluent was 0.0704 M. After that, a number of bulk experiments were carried out by applying different values of current density (20, 40 and 60 mA cm^{-2}) at 25 °C. As it can be observed from Fig. 1, when Na_2SO_4 was added in the effluent, color removal efficiency was significantly increased (curves b–d), achieving different values of HU (610, 152 and 0 HU after 12 h of electrolysis, for 20, 40 and 60 mA cm^{-2}, respectively). However, only at 40 and 60 mA cm^{-2}, the process showed fast decolorisation performances (97.9% and 100% of color removal, respectively); accomplishing Brazilian regulations (limit = 300 HU [20]) after 10 and 4 h, respectively (Fig. 1, curves c and d). The results obtained of electrochemical treatment to the variables studied (different applied current densities) in the present work, reflect that the solution conductivity affects cell potentials at constant current, favoring the electrogeneration of peroxodisulfates [1,15,17] increasing the efficiency in decolorization. It is important to remark that, adding Na_2SO_4, the solution pH decreased slightly during the electrolysis to values of 11.1–10.8, after that, pH is restored in the last phase of the electrochemical treatment to 12.

As already indicated by other authors [2,14,15,17,19,21,22], color removal is only indicative of dye fragmentation (chromophore group breaking); however, these pollutants can be converted in other more simple organic compounds [1]. For that reason, COD decay was also monitored when Na_2SO_4 was added by applying 20, 40 and 60 mA cm^{-2} of current density. Fig. 2 shows the influence of the current density on the COD decay during the electrochemical treatment of the real textile effluent, as a function of time, using BDD anode at 25 °C. Results clearly indicate that high COD removal was achieved by applying 60 mA cm^{-2} after 12 h of electrolysis (100% of COD removal). Instead, at 20 and 40 mA cm^{-2}, COD removal was not completed after 12 h of treatment, achieving no more than 75% and 92% of COD removal, respectively (Fig. 2). An important observation is that, increasing current density results in a higher charge consumed for complete mineralization due to a relative greater amount of •OH radicals wasted in parasite non-oxidizing reactions such as oxygen evolution reaction (o.e.r.) [2]. This behavior is characteristic of electrolyses under mass transport control that is performed applying a current higher than the
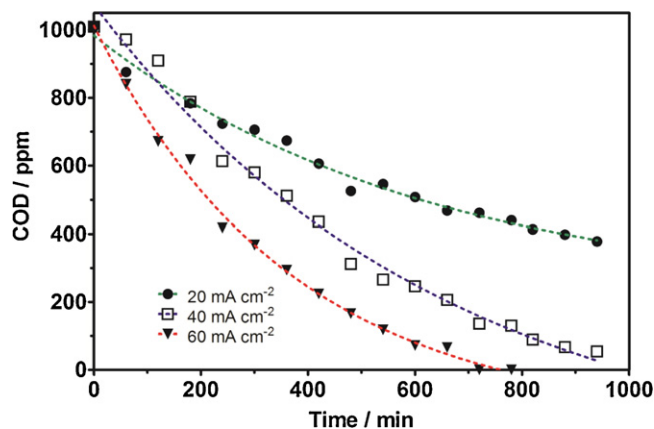

Fig. 2. Influence of applied current on the evolution of COD, as a function of time, during electrochemical treatment of actual textile effluent on BDD anode at different current densities. Conditions: T = 25 °C, 5 g of Na_2SO_4.

limiting one. Last assumption is in agreement with the results recently published by Panizza and Cerisola [23] and Martinez-Huitle et al. [2], during the anodic oxidation of a real carwash wastewater using lead dioxide (PbO_2) and diamond electrodes; and electrochemical treatment of real textile effluent using BDD anodes, respectively.

The effect of temperature during the electrochemical treatment of an actual textile effluent was also studied by applying 40 and 60 mA cm^{-2}, varying the temperature from 25 °C to 60 °C. The latter temperature was selected, because it mimics the real temperature of the textile industry discharges (60 °C). It was observed (Fig. 3) that changes in temperature have a strong influence on oxidation rate by applying 40 mA cm^{-2} and varying the temperature from 25 °C to 60 °C; since the COD removal after 9 and 10 h of treatment were 100% and 97% at 40 and 60 °C, respectively. While, COD removal rates (inset, Fig. 3) noticeably increased when 60 mA cm^{-2} was applied at 60 °C, reducing treatment time to 400 min. Previous studies on the oxidation of other organic pollutants using BDD anode have constantly reported that an increase of temperature favors organic oxidation; due to an increase of the activity of the anodes but this behavior is principally attributed to an increase of the indirect reaction of organics with electrogenerated oxidizing agents from electrolyte oxidation. In fact, electrolysis BDD anodes in aqueous media, containing chloride or sulphate ions,
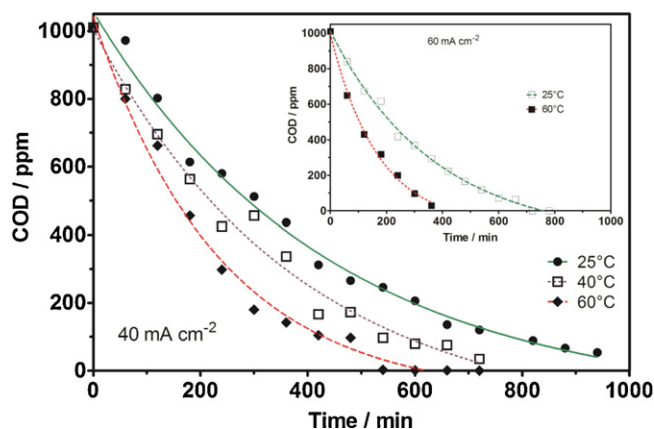

Fig. 3. Influence of temperature on the evolution of COD, as a function of time during oxidation of actual textile effluent on BDD anode. Conditions: j = 40 and 60 mA cm^{-2}; 5 g of Na_2SO_4.
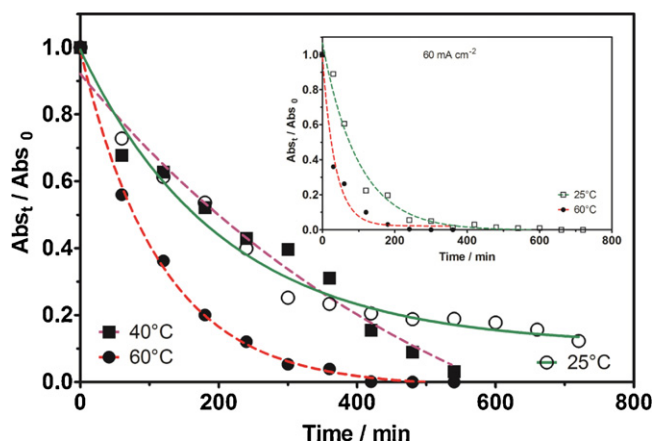
Fig. 4. Influence of temperature on the color removal, as a function of time during oxidation of actual textile effluent on BDD anode. Conditions: j = 40 and 60 mA cm^{-2}; 5 g of Na$_2$SO$_4$.

generates chlorine, peroxodisulphate (Eq. (1)) and hydrogen peroxide [2,15,17,24].

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (1)$$

These powerful oxidizing agents can oxidize organic matter by a chemical reaction whose rate with the amount of sulphate ions in solution or/and temperature [1,2,24–26]. Alternatively, if the production of strong oxidant species at higher temperatures is assumed, an increase in the decolorisation rate can be favored, as a consequence of the kinetics of volume oxidative reactions (in solution) to attack the chromophore group. In fact, complete color removal was favored at 40 and 60 °C, by applying 40 mA cm^{-2}, decreasing the treatment time up to 7 and 9 h, respectively (Fig. 4). Whilst, decolorisation rate becomes more rapidly when 60 mA cm^{-2} was applied at 60 °C (inset in Fig. 4), achieving complete decolorisation after 3 h of electrolysis-time respect to 7 h at 25 °C.

Another interesting feature of the sulphate mediated electrochemical treatment of effluent is the dependence on Na$_2$SO$_4$ concentration of the COD removal rate. Fig. 5 shows the influence of Na$_2$SO$_4$ concentration (in g dm^{-3}) as a function of the time during galvanostatic electrolysis of real textile wastewaters by applying 40 mA cm^{-2} of applied current density. And, as it was previously commented, the COD was poorly removed in absence of Na$_2$SO$_4$ in solution. However, COD removal rate increases significantly when the amount of Na$_2$SO$_4$ were added in solution in spite of that this increase was not significantly enhanced by an increase of Na$_2$SO$_4$
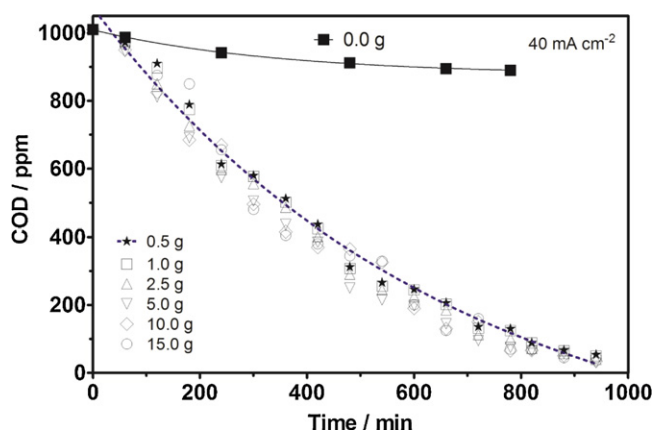

Fig. 5. Influence of Na$_2$SO$_4$ concentration on the COD removal, as a function of time; during oxidation of actual textile effluent on BDD anode, applying 40 mA cm^{-2}.
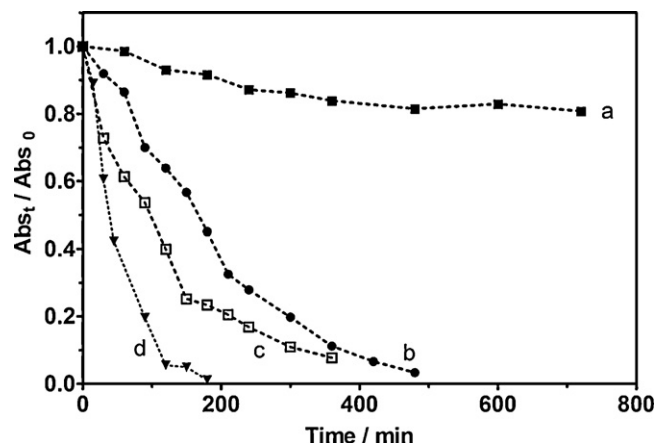

Fig. 6. Electrochemical decolorisation process of a real effluent, as a function of time, applying different current densities values at 25 °C (curve a: 60 mA cm^{-2}, effluent as obtained; curve b: 20 mA cm^{-2}, 5 g of NaCl; curve c: 40 mA cm^{-2}, 5 g of NaCl and curve d: 60 mA cm^{-2}, 5 g of NaCl.

concentration from 1 g to 15 g (Fig. 5). This outcome is in agreement with the figures already reported by Martinez-Huitle et al. [2].

For large scale application, as already demonstrated by Panizza and Cerisola [23] and Martinez-Huitle et al. [2], the estimation of the treatment costs, as a function of COD removal, is also a key point. Even if BDD have higher cell voltage, due to its higher overpotential for o.e.r., it has higher oxidation rate and consequently it consumed less energy (see Table 1) than other real effluents electrochemically treated using BDD anodes [2,23] (e.g. in the case of Na$_2$SO$_4$ (5 g in 0.5 L) 61.65 kWh m^{-3} (R$24.66; US$12.33), 44.92 kWh m^{-3} (R$17.97; US$8.98) and 35.60 kWh m^{-3} (R$14.24; US$7.12) for 25, 40 and 60 °C, respectively; by applying 40 mA cm^{-2}.

3.3. Electrochemical treatment of a real textile effluent using NaCl

In the case of NaCl, an amount of 5 g was added in the real effluent (0.5 L) in other words, the concentration of NaCl in the effluent was 0.171 M. After that, COD and color removal were investigated, analysing the effect of applied current density by applying 20, 40 and 60 mA cm^{-2} at 25 °C, while the temperature effect (40 and 60 °C) was studied under a current density of 40 mA cm^{-2}. On the other hand, several experiments were performed at 25 °C for studying the role of NaCl concentration during COD removal.

As it can be observed from Fig. 6 (curves b–d), when NaCl was added in the effluent, color removal efficiency was notably increased, decaying largely HU values than those obtained when Na$_2$SO$_4$ was employed (200, 25 and 0 HU after 6 h of electrolysis, for 20, 40 and 60 mA cm^{-2}, respectively). Conversely to Na$_2$SO$_4$, Brazilian regulations about color removal (fewer than 300 HU [20]) were attained, for all cases, after 6 h of treatment, when NaCl was used (Fig. 6). Then, dissolved salt has a strong influence on the results, and the removal efficiency is significantly improved with chloride medium [17,27]. These results were achieved due to the production of active chlorine species on BDD surface [19], favoring a quick elimination of color because these strong oxidant species rapidly attack the chromophore group [17,25].

In the case of elimination of organic matter, COD decays during Cl-mediated oxidation of the real textile effluent on BDD anode, as a function of time, at 25 °C, is showed in Fig. 7. As it can be observed, higher COD removal efficiencies were achieved at 20, 40 and 60 mA cm^{-2} of current density. Conversely to Na$_2$SO$_4$, before 10 h of electrolysis, more than 95% of COD removal was achieved, in all cases, achieving a lower charge consumed for complete mineralization. Theoretically, based on the existing literature

Table 1
Production of chloroform during electrochemical oxidation of real textile effluent using different Na_2SO_4 and NaCl concentrations. Energy consumption and cost for different experimental conditions.

Na_2SO_4 (g L^{-1})[a]/Molar	% COD removal[b]	Chloroform (ppm)	Energy consumption (kWh m^{-3})	Cost (Dollar[d]/Real[e])
0/0.000 M	12.5	–[c]	104.95	20.99/41.98
1/0.007 M	98	–[c]	68.02	13.60/27.20
2/0.014 M	100	–[c]	64.89	12.98/25.95
5/0.035 M	100	–[c]	62.52	12.50/25.01
10/0.070 M	100	–[c]	61.65	12.33/24.66
20/0.141 M	100	–[c]	60.53	12.11/24.21
30/0.211 M	100	–[c]	54.91	10.98/21.96

NaCl (g L^{-1})[a]/Molar	% COD removal[b]	Chloroform (ppm)	Energy consumption (kWh m^{-3})	Cost (Dollar[d]/Real[e])
0/0.000 M	12.5	–[c]	104.95	20.99/41.98
1/0.107 M	80	–[c]	53.76	10.75/21.50
2/0.034 M	95	45.0	49.92	9.98/19.97
5/0.086 M	100	65.6	43.82	8.76/17.53
10/0.171 M	100	83.6	36.96	7.39/14.26
20/0.341 M	100	126.9	24.36	4.87/9.74
30/0.513 M	100	150.1	16.40	3.28/6.56

[a] These values are consistent with the amounts used for 0.5 L in this work (0; 0.5; 1.0; 2.5; 5.0; 10.0 and 15.0 g).
[b] Removal efficiencies achieved at 25 °C and 40 mA cm^{-2}.
[c] Not detected.
[d] American currency.
[e] Brazilian currency.

[14,17,28–32], the electrochemical treatment can be carried out at lower potentials in the presence of chlorides, compared with those required for the direct anodic oxidation [30]. Then, the effluent conductivity was increased with the addition of NaCl, affecting the cell potentials promoting active chlorine species and favoring a faster COD and color abatement. On the other hand, the electrolysis in chloride media is strongly dependent on pH and its role must be considered.

The Cl-mediated oxidation of organic substrates has been widely investigated at Pt anodes and mechanism of the whole process has been proposed in the end of 90s [28–31] by De Battisti and co-workers studying the oxidation of glucose in the presence of chlorides. They have concluded that HClO is the oxidizing agent, formed at the anode, thanks to chloride oxidation and the concomitant oxygen evolution reaction. At the same time, both chloro- and oxychlororadicals, co-generated at the electrode surface and reacting in solution, have to be considered in the mechanism of the electrochemical destruction, thus representing an extension of the model initially proposed by Comninellis for the direct electrochemical oxidation. Then, in consideration of the fact that, in the case of chloride mediation, incineration reactions should be mainly a set of volume rather surface reactions, the change from Pt (by

the way also a "bad" catalyst for oxygen evolution reaction (o.e.r.)) to BDD should not involve dramatic changes in the incineration mechanism.

Reactions between water and radicals near the anode can yield molecular oxygen, free chlorine and hydrogen peroxide. Furthermore, hypochlorite can be formed as follows:

$$H_2O + Cl^- \rightarrow HOCl + H^+ + 2e^- \tag{2}$$

Therefore, direct anodic oxidation through results in reduced organic pollutants on real effluent as well as the formation of primary oxidants such as oxygen, chlorine, hypochlorite and hydrogen peroxide. Free chlorine and oxygen can further react on the anode yielding secondary oxidants such as chlorine dioxide and ozone, respectively. Primary and secondary oxidants are quite stable and migrate in the solution bulk where they indirectly oxidize the effluent. Therefore, COD removal efficiencies are achieved.

The efficiency of indirect oxidation depends on the diffusion rate of oxidants in the solution and on pH value [3,14,17,30]. At acidic conditions, free chlorine is the dominant oxidizing agent, while at slightly alkaline conditions hypochlorite, chloride ions and hydroxyl radicals are all important [3,30].

In this context, restricting now our analysis to solution pH, originally around 12.4, it decreases during the first two hours of electrolysis to values of 8–7, after that, pH around 10 is restored in the last phase of the electrochemical process (Fig. 7). Thus, ClO$^-$ will prevail in the first and third stage of the electrolysis, but HClO can be active at the electrode surface, in the intermediate region, as a consequence of the large acidity (pH is slightly acidic) due to the concomitant oxygen evolution, as indicated previously by other authors [30]. Based on these results, we can assume that the primary oxidation takes place at the chromophore group dye via chlorine species, after that, the opening of the rings is the second step of the electrochemical incineration/combustion. Thus, the production of species like hypochlorite and hypochlorous acid confirms that the oxidation of organic compounds dissolved in the effluent and by-products generated are oxidized in the bulk of the solution. Additionally, in consideration of the fact that the pH is restored at the end of the process, it is due to the elimination of carboxylic acids formed during treatment. These assumptions are confirmed with the results reported in Figs. 6 and 7, concerning to the decolorization and COD removal in chloride media. However, as previously pointed out by De Battisti and his group [30] and Polcaro
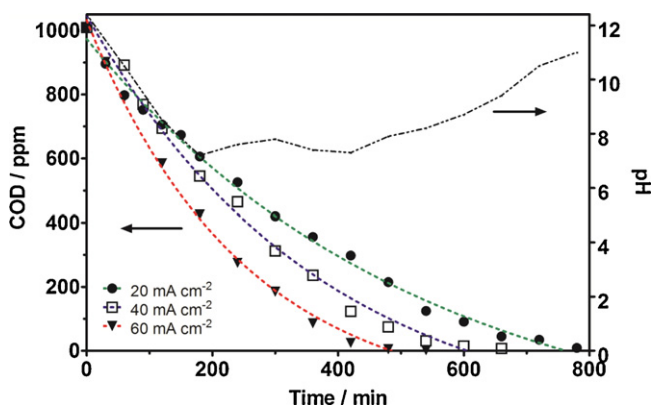

Fig. 7. Influence of applied current on the evolution of COD, as a function of time, during electrochemical treatment of actual textile effluent on BDD anode at different current densities. Conditions: T = 25 °C, 5 g of NaCl. Correlation between pH and COD removal during Cl-mediated oxidation.
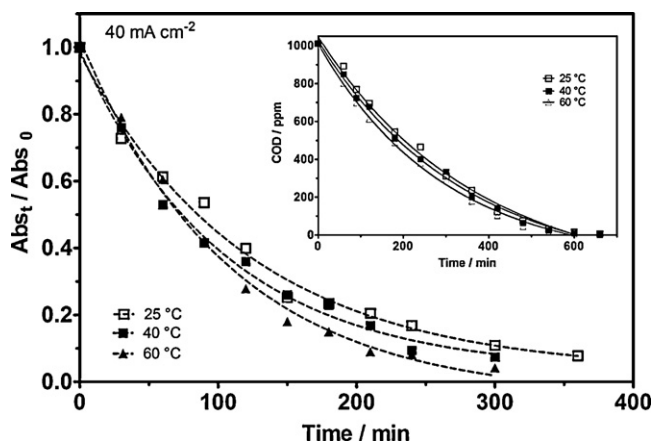
Fig. 8. Influence of temperature on the color removal, as a function of time and COD decrease (inset) during oxidation of actual textile effluent on BDD anode. Conditions: $j = 40\,mA\,cm^{-2}$; 5 g of NaCl.

et al. [18], the electrochemical oxidation of organic compounds in presence of high concentrated chlorides may results in a positive effect (higher removal rate) or may be in a undesired generation of chlorinated by-products. At this point, the study of intermediates formed during electrochemical treatment of this real effluent becomes a topic of great importance in this research, that will be discussed in the next section.

Assuming that the rate of the each reaction must be dependent on temperature, as already demonstrated by other authors [28,30], we decided to study the effect of an increase of temperature during Cl-mediated oxidation. During electrochemical experiments at 40 and 60 °C by applying current densities of 40 and 60 mA cm^{-2}, complete color removal was accomplished, however, an slight increase in decolorisation rate was observed when temperature was increased (see Fig. 8, showing data only for 40 mA cm^{-2}). In the case of 60 mA cm^{-2}, decolorisation rate becomes faster due to the increase in the current density even when the behavior of color decay was very similar for all temperatures (data no shown).

The temperature effect on COD abatement was insignificant, during Cl-mediated oxidation. COD removal rates were similar at all temperatures used, employing analogous treatment times than those achieved at 25 °C (see inset in Fig. 8, showing data only for 40 mA cm^{-2}). It can be assumed that, of two competitive reactions: o.e.r. and chlorine evolution reaction (chl.e.r.), the increase of temperature favors the one with higher activation energy (o.e.r.) which necessarily involves more or less pronounced decrease in incineration rate, because less of active chlorine is formed at one and the same current density [28]. Consequently, the small effect on Cl-mediated electrochemical oxidation reflects some compensation between electrochemical and chemical reactions when the temperature was increased.

Regarding on the effect on NaCl concentration used during mediated oxidation, different concentrations of chloride were added in solution. Fig. 9 shows the influence of NaCl concentration (in g dm^{-3}) as a function of the time during galvanostatic electrolysis of real textile wastewaters (by applying 40 mA cm^{-2}). When an increase on NaCl concentration was attained, COD removal becomes faster. Interestingly, the mediated process does not depend on applied current density, but it depends on NaCl concentration. However, as hypothesized by other authors and not confirmed by them [14,17], recalcitrant intermediates can be formed in the chloride medium, most probably organochloride compounds. For this reason, the identification of intermediates formed by using NaCl must be studied, focusing in chlorinated by-products.
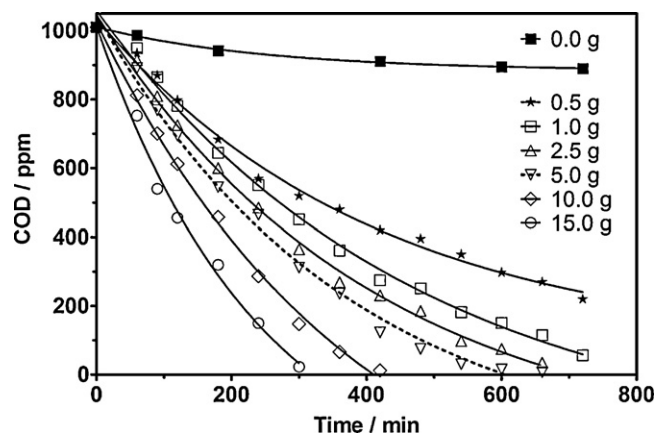

Fig. 9. Influence of NaCl concentration on the COD removal, as a function of time; during oxidation of actual textile effluent on BDD anode, applying 40 mA cm^{-2}.

For the case of Cl-mediated oxidation, the estimation of the treatment costs (Table 1), as a function of COD removal were about 36.96 kWh m^{-3} (R\$14.78; US\$7.39), 34.80 kWh m^{-3}(R\$13.92; US\$6.96) and 32.16 kWh m^{-3}(R\$12.86; US\$6.43) for 25, 40 and 60 °C, respectively; by applying 40 mA cm^{-2}; justifying the use of this treatment in terms of economic alternative treatment and time.

3.4. Final by-products identification

In the previous work [1], during the electrochemical oxidation of synthetic dyes wastewaters (Remazol Red BR (RRB) and Novacron Blue C-D (NB)) using a BDD anode different by-products were identified by means of gas chromatography/mass spectrometry (GC/MS) technique, such as 4,4-N,N-dimethyl aniline, aniline, benzoic acid, hydroquinone, acetic, formic and oxalic acids for NB degradation, while other intermediates such as 2-hydroxy benzoic acid, dimethyl aniline and 1,4-dihydroxy benzene, phenol, benzoic acid, acetic, formic and oxalic acids were identified for RRB degradation. Therefore, the identification of the final by-products formed during electrochemical treatment of a real textile effluent, by strong oxidant species, can be considered a crucial point to reveal the applicability of this alternative technology for the depuration of this kind of wastewaters. Consequently, at the end of each electrochemical experiment, at different current densities and temperatures, samples of real textile effluent electrochemically treated were withdrawn and analyzed by GC/MS technique.

For the oxidation of real textile effluent using Na$_2$SO$_4$, similar intermediates detected in the previous work were identified, but with minor concentration:

- at 60 mA cm^{-2} only oxalate/oxalic acid was detected;
- at 40 mA cm^{-2}, intermediates such as benzoic acid, hydroquinone, acetic and oxalic acids;
- at 20 mA cm^{-2}, more by-products, such as phenol, benzoquinones, aliphatic acids (acetic, oxalic, propionic and butyric acids), RRB and NB dyes, were detected.

Whereas, when an increase in the temperature was achieved (40 and 60 °C), some traces of aliphatic acids were detected (acetic and oxalic acids), in both cases. This behavior is in agreement with COD decay, where a quasi-complete elimination was attained by applying 40 or 60 mA cm^{-2} (Fig. 3) at different temperatures.

Considering the by-products formed under different experimental conditions, it can be assumed that the presence of sulfates ions lead to occurrence of peroxodisulfates in a zone very close

to the anode surface and after, in the bulk solution peroxodisulfates; allowing the degradation of organic matter dissolved on real textile effluent by attacking via ROS and peroxodisulfates with a consequent transformation (by-products) up to quasi-complete degradation (CO_2, carboxylic acids and water). Nevertheless, as it has been previously reported in the literature [2,23], a notable production of peroxodisulfates is achieved at higher temperatures, and the kinetics of volume oxidative reactions becomes important (as confirmed by using the I_2/I^- titration for detection of peroxodisulfates in solution), increasing the mineralization rate of the electrolytic process, producing traces of by-products. These figures are in divergence with the assumptions suggested by Aquino et al. [17] where they concluded that the concentration range of Na_2SO_4 used in their study (14.204 g/L) did not lead to the occurrence of oxidants in the bulk electrolyte.

During the sample analysis by GC/MS technique, for the electrolysis in presence of chlorides (0.171 M), a minor number of intermediates was detected, such as phenol, chlorobenzene, 2-hydroxy benzoic acid and 1,4-dihydroxy benzene. The attack of chloro-oxidant species [18,30,32] at the site of the azo bond and terminal N,N dimethyl chain results in the formation of above intermediates. Chlorobenzene might result from the chlorination of benzene or phenol. Also, GC/MS analysis reveals the presence of chloroform.

It is important to remark that, the presence of chlorobenzene in the absence of chlorophenols, and also that the presence of chloroform in the absence of other chlorinated precursors, seems to suggest that both, chlorobenzene and chloroform might be related with some gas-phase reactivity along the complex analytical path itself, rather than to reactions at/near electrode (anode) surface in aquatic media, opening the possibility of the use of BDD anodes for Cl-mediated oxidation under specific conditions of NaCl concentration.

On the other hand, results obtained during the variation of the temperature showed that a rapid mineralization (with very small concentration of intermediates) is promoted, but with final recalcitrant intermediate formed; chloroform. These figures suggest that dangerous chlorinated by-products are being formed when NaCl is used.

From the data discussed above, it can be inferred that the degradation process when sulfate is added occurs with significant formation of intermediates but without occurrence formation of organochlorate compounds. Whereas oxidants formed during Cl-mediated oxidation reduce remarkably the formation of intermediates but it favors the generation of organochlorinated compounds (complicating the complete oxidation), and a number of these by-products are a major health concern because of their carcinogenic properties [33–35]. These outcomes are in discrepancy with the assumptions reported by Aquino et al. [17] where they commented that the degradation processes in sulfate medium occurs with no significant formation of intermediates, while active chlorine species contribute significantly to the oxidation of the dyes and their intermediates, including organochloride compounds.

Another important observation is the persistent presence of chloroform, one of the most common chemical by-products of water disinfection and wastewater treatment [33]. Several researches have demonstrated that it causes cancer in laboratory animals when administered at very high doses [34,35]. Then, the scientific issue concerns whether there is a dose below which chloroform is safe. Therefore, it is important to answer the follow question: what is the amount of this organic compound at different NaCl used for treating real effluent?

From the data reported in Table 1, it can be inferred that increasing the concentration of chloride ions in solution, higher COD removal efficiencies were achieved but an increase in formation of chloroform is accomplished. Considering that 50 ppm is the permissible exposure limit, only for lower concentrations of NaCl no traces of chloroform were detected. Conversely, using Na_2SO_4, no production of organochloride compounds was achieved, obtaining higher COD removal efficiencies.

3.5. Comparison of the processes un-addition salts, sulphate addition and chloride addition

The results obtained of effluent electrochemical treatment to the variables studied (un-addition salts, sulphate addition and chloride addition), in the present work, have showed that the •OH-based mechanism of incineration should work largely independent from electrolyte nature (un-addition salts), unless the electrolyte itself takes part in the whole process (sulphate and chloride addition), see Figs. 1, 2, 6 and 7. In cases of sulphate and chloride-mediated oxidation, the electrogeneration of strong oxidants: peroxodisulfates ions in case of sulphate solutions, and hypochlorite, hypochlorous acid, chlorine dioxide, in the case of chloride solutions, the reactions in the bulk solution via these oxidant species becomes important and the effect of temperature could be expected according to the Arrhenius approach. Peroxodisulphates can be formed in solutions containing sulphates, especially at higher temperatures (60 °C), during electrolysis with BDD electrodes. These reagents are very powerful oxidants and can oxidize organic matter leading to an increase in color removal rates and COD decay. Therefore, a complete color removal was attained at 60 °C more rapidly than that other conditions (Fig. 6); while complete COD decay was achieved after 6 h treated by electrochemical process (inset, Fig. 6) respect to 12 h at 25 °C. Conversely to Na_2SO_4, higher COD and color removal efficiencies were achieved by Cl-mediated oxidation. Complete color removals were attained, for all cases, after 6 h of treatment, when NaCl was used, and before 10 h of electrolysis, more than 95% of COD removal was achieved.

The behaviors observed in the cases of sulphate and chloride mediated oxidation, during COD and color removals, show that is radically dependent on mediator, with respect to the •OH incineration. While the electrogeneration of peroxodisulfates favors a faster electro-conversion/combustion than that observed at •OH-based mechanism of incineration; it is interesting the possibility of improving the efficiency of the electrochemical treatment by chloride mediated process via active chlorine. Although ClO^- and HClO are strong oxidant agents; their effect on COD abatement through volume reactions is limited by pH and chloride concentration in solution. The production of chloro and oxy-chloro radicals at the anode surface plays a decisive role, and their reactivity as a function of metal oxide electrode has been discussed by De Battisti and co-workers [30] in terms of interactions with the surface oxide lattice, and by Polcaro and co-workers in terms of strong species produced on BDD surface [18]. Then, the above approaches can be applied to the active chlorinate mediation and the scheme proposed by De Battisti can be adapted to the case of BDD anode (Fig. 10), remembering that in the case of chloride mediation, incineration reactions should be mainly a set of volume rather surface reactions.

From an industrial point of view, in the case of sulphates, only a small amount Na_2SO_4 can be added to the effluent to favor the complete removal of dissolved organic matter (Fig. 5). Whereas, a considerable amount of NaCl is traduced in a more efficient COD removal (Fig. 9). Nevertheless, it favors the generation of organochlorinated compounds at the end of the mediated treatment. However, GC-MS data about the presence of signals related to organic chloro compounds seem to exclude the insertion of chlorine atoms at/near BDD surface due to no presence of organic precursors.
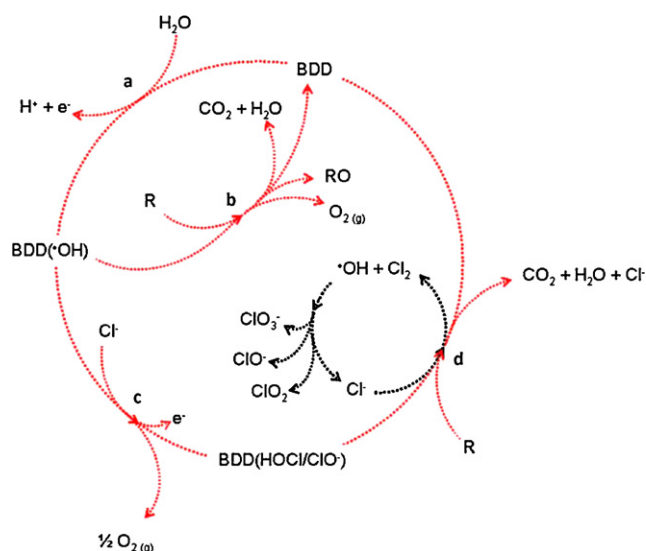
Fig. 10. Simplified diagram for $^{\bullet}$OH mechanism oxidation (adaptation from Comninellis model [36]) and Cl-mediated oxidation (adaptation from De Battisti model [30]) using BDD anodes: (a) water discharge to hydroxyl radicals, (b) anodic oxidation of organic compounds (electrochemical combustion/conversion) via hydroxyl radicals with simultaneous oxygen evolution, (c) chloride conversion to active chlorine species on BDD surface with simultaneous oxygen evolution, (d) production of active chlorine species by reaction with OH radicals in solution and chemical combustion/conversion of the organic compound via active chlorine species.

Even though BDD oxidation is very effective (in both cases), its energy consumption is relatively higher for useful application as the only treatment process; but it could be used as a pre-treatment of a cleansing technology divided in two step processes consisting in an electrochemical treatment followed by biological depuration or vice versa. It is important to remark that, even when the use of NaCl reduced notably the costs, the addition of NaCl to the effluent must be limited by formation of undesired by-products. These data are reported in Table 1 in order to increase the information of this alternative treatment proposed here.

As an additional environmental point of view, the use of NaCl during electrochemical treatment of real effluents must be perfectly monitored and limited due to the electrogeneration of undesirable by-products, sometimes more dangerous than those in the beginning of the treatment, according the by-products identified in this work.

4. Concluding remarks

On basis of the results obtained for anodic oxidation of a real textile effluent, the electrochemical technology can be suitable as an alternative for pre-treatment under the real discharge conditions (COD, pH 10 and temp = 60 $^{\circ}$C) with the addition of a small amount of Na_2SO_4 or NaCl. Using these salts, COD and color were efficiently reduced before 12 h of electrochemical treatment, attaining Brazilian legal requirements. Considering that in the Brazilian Textile industry, complete COD and color removal are accomplished after 5 or 6 days of biological depuration coupled with a subsequent physical–chemical treatment (under specific pH and temperature conditions); the electrochemical treatment could be considered as a promising alternative.

The use of Na_2SO_4 or NaCl favors the production of strong oxidant species that together to ROS (such as, hydroxyl radicals) oxidize dissolved organic matter in real textile effluent (close to anode surface and in the reaction cage). However, each effluent is different, for that reason, when different dosages of NaCl are used; different chloroform concentrations could be produced and

detected. Perhaps the production of undesired by-products, such as organochloride compounds, can vary and it depends on NaCl concentration added to the real effluent. Then, particular attention and experimental observations must be taken into consideration before or during its use; and future studies by other authors must report it.

Finally, the results reported in Ref. [2] and in the present work have recently allowed to start the design and implementation of a pilot industrial–electrochemical cell in the textile industry. These experiments are in progress and their results will be reported in detail in a separate paper in a near future.

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